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Note

Facile exchange of glycosyl *S*,*S*-acetals to their *O*,*O*-acetals and preparation of glycofuranosides from acyclic glycosyl *S*,*S*-acetals under metal-free reaction conditions in the presence of 1,3-dibromo-5,5-dimethylhydantoin☆

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Abstract—Exchange of acyclic glycosyl dithioacetals to their *O*,*O*-acetals has been achieved by a generalized reaction protocol mediated by 1,3-dibromo-5,5-dimethylhydantoin under mild, metal-free and neutral conditions. This methodology has been extended to the synthesis of alkyl glycofuranosides.

Keywords: 1,3-Dibromo-5,5-dimethylhydantoin; Glycofuranosides; Acyclic sugar dithioacetals

Dithioacetals are attractive protecting groups for carbonyl functionalities in the total synthesis of complex natural products,[1,2] but their robust nature sometimes makes deprotection difficult. There are several literature precedents for the deprotection of dithioacetals, which can be used as needed during the synthesis of natural products.[3] Besides the above mentioned applications, dithioacetals are also important intermediates in the synthesis of the corresponding *O*,*O*-acetals. A few literature reports are available for the exchange of *S*,*S*-acetals to *O*,*O*-acetals, most of which involve the use of toxic heavy metal salts, such as $HgCl_2$, HgO or expensive reagents.[4–6] Therefore, the development of a mild, efficient, nontoxic, metal-free conditions would extend the scope of this conversion.

Acyclic glycosyl dithioacetals were first prepared by E. Fischer in the last century,[7,8] and as such, represent some of the oldest known carbohydrate derivatives. These classes of compounds are easily prepared in high yield and offer a convenient starting point for preparing other acyclic as well as furanoside, pyranoside and septanoside derivatives of sugars.[9–11] Recently, we have found that 1,3-dibromo-5,5-dimethylhydantoin (DBDH) can act as a thiophilic activator to convert dithioacetals to the corresponding aldehydes.[12] DBDH is well known for its ability to act as a free radical brominating agent[13] or as a source of bromonium ion and has been exploited in aromatic ring bromination.[14] DBDH has also been used to convert dithioacetals into *gem*-difluorides.[15,16] We have envisioned that DBDH might be a useful catalyst for the conversion of *S*,*S*-acetals to *O*,*O*-acetals under anhydrous reaction conditions and thus could provide a metal-free reaction protocol for such transformations. In this communication, we report the DBDH-mediated activation of glycosyl dithioacetals to form glycosyl *O*,*O*-acetals and glycofuranosides. A related methodology has appeared in the literature, which describes the cleavage of glycosyl acetals and dithioacetals using iodine in methanol.[17] We have applied iodine for the exchange of dithioacetals to their *O*,*O*-acetals and in every case conversion of the dithioacetals to the parent aldehydes was observed without formation of *O*,*O*-acetals. In the case of glycofuranoside formation, use of iodine requires much longer

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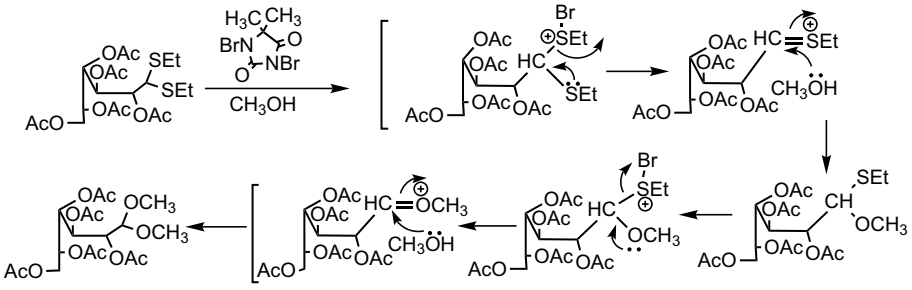


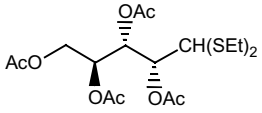
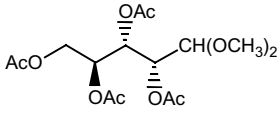
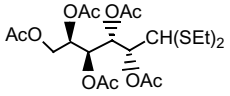
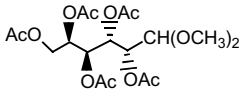
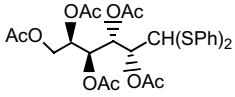
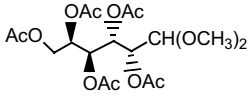
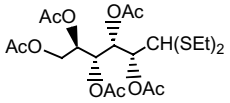
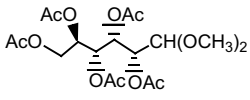
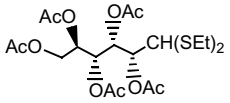
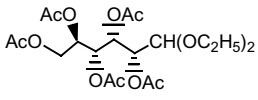
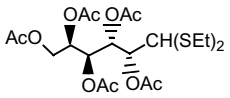
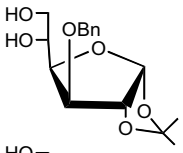
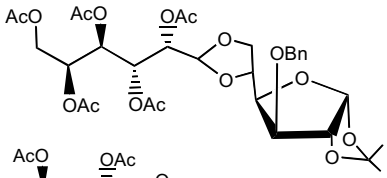
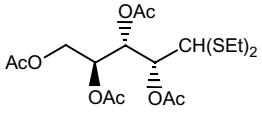
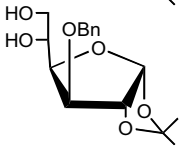
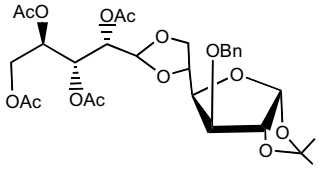
Scheme 1.

reaction time (~48 h) compared to DBDH-mediated reaction conditions, which generates glycofuranosides within a few minutes. In addition, considerable quantities of glycopyranosides were formed when using iodine, which does not occur with DBDH activation.

To probe the scope of the DBDH-mediated transformation, a series of per-*O*-acetylated acyclic glycosyl dithioacetals were treated with anhydrous alcohols or dihydroxy monosaccharide derivatives in the presence of DBDH (Scheme 1). As expected, both cyclic and acyclic *O*,*O*-acetals of per-*O*-acetylated acyclic sugars were obtained in very good yield (Table 1). Formation of the products was confirmed by NMR and mass spectral data (see Experimental).

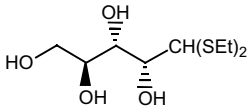
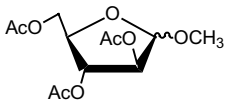
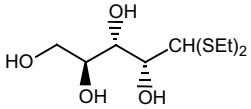
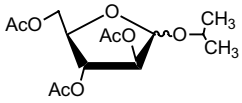
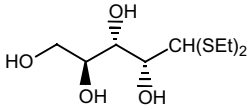
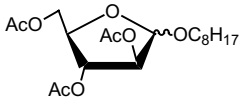
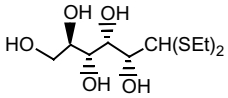
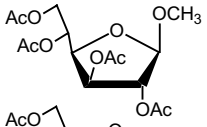
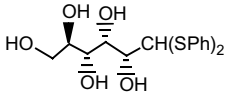
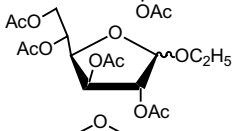
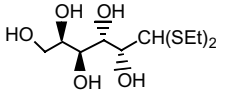
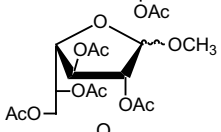
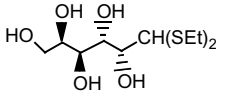
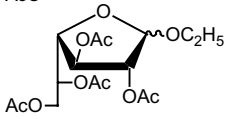
This methodology has been further extended to the synthesis of alkyl glycofuranosides. Furanosidic sugars are widely abundant in the cell wall of pathogenic bacteria,[18–20] for example, various *Mycobacteria*, fungi including the members of the genera *Aspergillus* and *Penicillium*[21] and pathogenic protozoa[22,23] such as *Trypanosoma cruzi* and certain *Leishmania* species. Therefore, carbohydrate haptens containing furanosides moieties could be useful for designing bacterial cell-wall biosynthesis inhibitors as well as for the preparation of

Table 1. Conversion of dithioacetals to *O*,*O*-acetals in the presence of DBDH

Entry	Dithioacetal (**1**)	Alcohols	*O*,*O*-acetals (2)	Time (min)	Yield[a] (%)
a		CH_3OH		30	90
b		CH_3OH		40	85
c		CH_3OH		40	90
d		CH_3OH		45	88[7,8]
e		C_2H_5OH		40	85
f				60	75
g				60	80

[a] Isolated yield.

Table 2. Conversion of acyclic glycosyl dithioacetals to alkyl glycofuranosides in the presence of DBDH

Entry	Dithioacetal (**1**)	Alcohols	Per-*O*-acetylated glycofuranosides (**3**)	Time (min)	Yield (%) [β:α][a]
a		CH_3OH		30	86 [1:11][25]
b		$(CH_3)_2CHOH$		60	80 [1:3.5][26]
c		$C_8H_{17}OH$		45	75 [1:5.5][27]
d		CH_3OH		30	82 [1:0][28]
e		C_2H_5OH		30	85 [4:1][29]
f		CH_3OH		30	90 [9:1][9]
g		C_2H_5OH		25	78 [13:1][9]

[a] Isolated yield. Ratio was determined by comparing the integration values of inseparable mixture of two isomers in NMR spectra.

artificial carbohydrate antigens for vaccine generation. Earlier methods for the conversion of dithioacetals to glycofuranosides involved the use of toxic mercury salts.[10] Therefore, a metal-free method for this transformation could be beneficial to the existing protocols. Thus, acyclic glycosyl dithioacetals were treated with a series of alcohols in the presence of DBDH in DMF as solvent to furnish several alkyl glycofuranosides in very good yield (Table 2). In most cases, the formation of alkyl furanosides from acyclic glycosyl dithioacetals resulted in a mixture of α- and β-isomers, the ratio of which was determined by comparing the integration values of the peaks in the NMR spectra of the inseparable mixture. The glycofuranosides were characterized by ^1H NMR, ^{13}C NMR, HPLC and NOE experiments. In all cases, formation of pyranosidic glycosides was not observed. The present reaction condition may be considered as a metal-free, nontoxic alternative to the previous methods for the preparation of alkyl glycofuranosides.

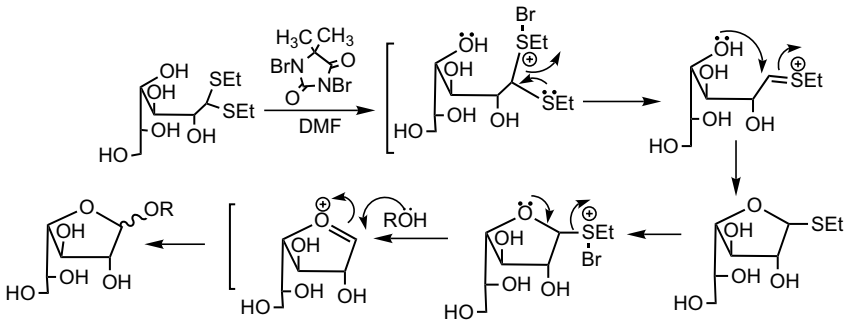
We presume that 1,3-dibromo-5,5-dimethylhydantoin produces active bromonium ion (Br^+) and forms a sulfonium ion intermediate from the dithioacetal, which smoothly forms an *O*,*O*-acetal in presence of an alcohol (Scheme 1). In the case of glycofuranoside formation, we propose that the product is formed by intramolecular nucleophilic attack from the hydroxyl group at C-4 followed by a nucleophilic attack of the alcohol at C-1 (Scheme 2).

In conclusion, the present method provides a fast, efficient and selective protocol for the conversion of acyclic glycosyl dithioacetals into their corresponding *O*,*O*-acetals. Due to the stability of DBDH to water, no extra care is needed during the handling of the reagent. The preparation of alkyl glycofuranosides is an important application of this methodology, which has been demonstrated for the first time under a metal-free reaction conditions. Operational simplicity, reduced toxicity, exceptionally fast rate of formation of *O*-acetals and alkyl glycofuranosides under mild reaction conditions without requirement of any extra additive makes this an attractive alternative to existing methodology. Studies on stereoselective glycosylation reaction using 1,3-dibromo-5,5-dimethylhydantoin is currently in progress in our laboratory.

1. Experimental

1.1. General methods

The general methods are same as used previously.[24] 1,3-Dibromo-5,5-dimethylhydantoin was purchased from Aldrich Chemical company.



Scheme 2.

1.2. Typical experimental protocol for the preparation of *O*,*O*-acetals from dithioacetals

To a solution of dithioacetal (1.0 mmol) in anhydrous CH_3OH (5.0 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (286.0 mg, 1.0 mmol) at 0 °C and the reaction mixture was allowed to stir for appropriate time (Table 1). After completion of the reaction, the mixture was concentrated under reduced pressure at low temperature and the concentrate was diluted with CH_2Cl_2 and washed with 5% aq $Na_2S_2O_3$, aq $NaHCO_3$ and water successively, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified on silica gel using mixtures of hexane and EtOAc as the eluant.

1.3. Typical procedure for the preparation of alkyl glycofuranosides from acyclic glycosyl dithioacetal

To a solution of glycosyl dithioacetal (1.0 mmol) in dry DMF (2.0 mL) was added anhydrous CH_3OH (60 μL; 1.5 mmol) followed by 1,3-dibromo-5,5-dimethylhydantoin (286.0 mg, 1.0 mmol) at room temperature and the reaction mixture was allowed to stir for appropriate time (Table 2). After completion of the reaction, the mixture was concentrated under reduced pressure at low temperature. The crude reaction mixture was acetylated using Ac_2O and pyridine and the per-acetylated alkyl glycofuranosides were purified on silica gel using mixtures of hexane and EtOAc as the eluant. Spectral data for the per-*O*-acetylated alkyl glycofuranosides are provided.

1.4. 2,3,4,5-Tetra-*O*-acetyl-D-arabinose dimethyl acetal (2a)

IR (neat): 2944, 1750, 1440, 1373, 1221, 1074, 976 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.06–2.12 (4s, 12H, $4COCH_3$), 3.32, 3.37 (2s, 6H, $2OCH_3$), 4.12 (ddd, 2H), 4.30 (d, $J = 6.8$ Hz, 1H), 5.12 (m, 1H), 5.24 (dd, $J = 7.5$, 4.0 Hz, 1H), 5.49 (dd, $J = 8.0$, 4.0 Hz, 1H); ^{13}C NMR: δ 20.9 (3C), 21.0, 52.2, 55.5, 63.4, 68.0 (2C), 68.5, 102.0, 169.6, 170.0, 170.1, 170.8; $[\alpha]_D$ +20.6 (*c* 1.5, $CHCl_3$); *m*/*z*: 363 [M−1]. Anal. Calcd for $C_{15}H_{24}O_{10}$ (364): C, 49.45; H, 6.64. Found: C, 49.37; H, 6.75.

1.5. 2,3,4,5,6-Penta-*O*-acetyl-D-galactose dimethyl acetal (2b)

IR (neat): 3473, 2933, 2856, 1745, 1596, 1446, 1374, 1217, 1050, 958, 859, 686, 621 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.00–2.13 (5s, 15H, $5COCH_3$), 3.29, 3.34 (2s, 6H, $2OCH_3$), 3.78 (dd, 1H), 4.20 (d, $J = 6.6$ Hz, 1H), 4.25 (dd, 1H), 5.14 (dd, 1H), 5.21 (m, 2H), 5.49 (dd, 1H); ^{13}C NMR: δ 21.0 (3C), 21.1 (2C), 53.6, 55.6, 62.7, 67.9, 68.0, 68.1, 68.2, 102.3, 169.6, 170.3, 170.7, 170.8 (2C); $[\alpha]_D$ +18 (*c* 1.3, $CHCl_3$); *m*/*z*: 405 [M−OCH_3]. Anal. Calcd for $C_{18}H_{28}O_{12}$ (436): C, 49.54; H, 6.47. Found: C, 49.47; H, 6.55.

1.6. 2,3,4,5,6-Penta-*O*-acetyl-D-glucose dimethyl acetal (2d)

IR (neat): 2927, 2851, 1752, 1440, 1372, 1225, 1122, 1076, 956, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.04–2.13 (5s, 15H, $5COCH_3$), 3.28, 3.42 (2s, 6H, $2OCH_3$), 4.09 (ddd, 2H), 4.11 (d, $J = 6.0$ Hz, 1H), 5.08 (m, 1H), 5.17 (m, 1H), 5.39 (m, 1H), 5.50 (m, 1H); ^{13}C NMR: δ 20.8 (2C), 21.0 (3C), 54.1, 56.5, 62.0, 69.0, 69.2, 69.7, 70.2, 102.8, 169.9 (2C), 170.2 (2C), 170.8; $[\alpha]_D$ +14 (*c* 1.2, $CHCl_3$); *m*/*z*: 405 [M−OCH_3]. Anal. Calcd for $C_{18}H_{28}O_{12}$ (436): C, 49.54; H, 6.47. Found: C, 49.47; H, 6.56.

1.7. 3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6-*O*-(2,3,4,5,6-penta-*O*-acetyl-D-galactosylidene)-α-D-glucofuranose (2f)

IR (neat): 3470, 2962, 2923, 1745, 1588, 1453, 1374, 1225, 1122, 1081, 1035, 959, 855, 746, 703 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.29, 1.48 (2s, 6H, $CH(CH_3)_2$), 2.01–2.12 (5s, 15H, $5COCH_3$), 3.93 (m, 4H), 4.02 (m, 2H), 4.26 (m, 2H), 4.54 (d, $J = 3.6$ Hz, 1H), 4.60 (s, 2H, $PhCH_2$), 4.96 (d, $J = 3.4$ Hz, 1H), 5.32 (m, 2H), 5.60 (d, $J = 7.6$, 1.2 Hz, 1H), 5.88 (d, $J = 3.5$ Hz, 1H), 7.32–

7.34 (m, 5H, aromatic); ^{13}C NMR: δ 21.0 (2C), 21.1 (3C), 26.6, 27.2, 54.3, 67.5, 67.9, 68.1, 68.7, 73.0, 73.5, 80.9, 82.1 (2C), 82.9, 102.4, 105.7, 112.3, 127.9–137.9 (aromatic), 169.8, 170.1, 170.2, 170.5, 170.6; $[\alpha]_D$ −42 (*c* 1.2, $CHCl_3$); ESI-MS: 682 (M, calcd); 700.4 ($M+NH_4^+$, found). Anal. Calcd for $C_{32}H_{42}O_{16}$: C, 56.30; H, 6.20. Found: C, 56.19; H, 6.35.

1.8. 3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6-*O*-(2,3,4,5-tetra-*O*-acetyl-D-arabinosylidene)-α-D-glucofuranose (2g)

IR (neat): 3023, 2986, 2935, 1745, 1455, 1374, 1218, 1163, 1076, 1046, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.30, 1.47 (2s, 6H, $CH(CH_3)_2$), 1.99–2.11 (4s, 12H, $4COCH_3$), 3.99 (m, 1H), 4.10 (m, 3H), 4.22 (m, 1H), 4.30 (m, 1H), 4.52 (m, 1H), 4.63 (m, 2H), 4.98 (d, *J* = 3.6 Hz, 1H), 5.10 (m, 3H), 5.51 (dd, *J* = 7.6, 2.6 Hz, 1H), 5.88 (t, *J* = 7.6 Hz each, 1H), 7.32–7.36 (m, 5H, aromatic); ^{13}C NMR: δ 21.0 (4C), 26.6, 27.2, 62.1, 67.9, 68.6, 68.9, 70.1, 72.8, 73.4, 80.9, 82.1, 83.1, 102.0, 105.7, 112.3, 127.9–138.0 (aromatic), 169.8, 170.1, 170.2, 170.9; $[\alpha]_D$ −25 (*c* 1.3, $CHCl_3$); ESI-MS: 610 (M, calcd); 628.3 ($M+NH_4^+$, found). Anal. Calcd for $C_{29}H_{38}O_{14}$: C, 57.04; H, 6.27. Found: C, 56.90; H, 6.45.

1.9. Methyl 2,3,5-tri-*O*-acetyl-α-D-arabinofuranoside (3a)

IR (neat): 3023, 2941, 1748, 1441, 1372, 1222, 1110, 1051, 954, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.10, 2.12 (2s, 9H, $3COCH_3$), 3.40 (s, 3H, OCH_3), 4.13–4.24 (m, 2H, H-$5_{a,b}$), 4.39–4.49 (m, 1H, H-4), 4.93 (br s, 1H, H-1), 4.98–5.02 (dd, *J* = 6.0, 1.4 Hz, 1H, H-3), 5.07 (d, *J* = 1.4 Hz, 1H, H-2); ^{13}C NMR ($CDCl_3$): δ 21.0 (3C), 55.3, 63.6, 76.8, 80.6, 81.6, 107.1, 169.9, 170.5, 170.9; $[\alpha]_D$ +48 (*c* 1.6, $CHCl_3$); *m*/*z*: 291 [M+1]. Anal. Calcd for $C_{12}H_{18}O_8$ (290): C, 49.65; H, 6.25. Found: C, 49.57; H, 6.32.

1.10. Isopropyl 2,3,5-tri-*O*-acetyl-α-D-arabinofuranoside (3b)

IR (neat): 2976, 2936, 1744, 1438, 1372, 1231, 1039, 979, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.15, 1.18, 1.20, 1.25 (4s, 6H, $CH(CH_3)_2$), 2.08, 2.10, 2.11 (3s, 9H, $3COCH_3$), 3.80–4.05 (m, 1H, $CH(CH_3)_2$), 4.20–4.28 (m, 2H, H-$5_{a,b}$), 4.36–4.48 (m, 1H, H-4), 4.94–4.98 (m, 1H, H-3), 5.03 (d, *J* = 1.5 Hz, 1H, H-2), 5.12 (br s, 1H, H-1); ^{13}C NMR: δ 20.8, 21.1, 21.7, 23.6 (2C), 63.7, 69.7, 77.4, 80.2, 82.2, 104.2; $[\alpha]_D$ +26.9 (*c* 1.3, $CHCl_3$); *m*/*z*: 319 [M+1]. Anal. Calcd for $C_{14}H_{22}O_8$ (318): C, 52.82; H, 6.97. Found: C, 52.74; H, 7.12.

1.11. Octyl 2,3,5-tri-*O*-acetyl-α-D-arabinofuranoside (3c)

IR (neat): 2930, 2861, 2374, 1748, 1372, 1230, 1049 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, octyl), 1.27 (m, 10H, octyl), 1.57 (m, 2H, octyl), 2.09, 2.10 (2s, 9H, $3COCH_3$), 3.36–3.50 (m, 1H), 3.63–3.77 (m, 1H), 4.21–4.26 (m, 2H), 4.38–4.47 (m, 2H), 4.96–5.02 (m, 2H), 5.07 (br s, 1H); ^{13}C NMR: δ 14.3, 20.8 (2C), 21.0, 22.9, 26.3, 29.5 (2C), 29.7, 32.1, 63.7, 67.9, 77.6, 80.5, 81.7, 105.9, 169.9, 170.4, 170.8; $[\alpha]_D$ +16.3 (*c* 1.5, $CHCl_3$); *m*/*z*: 389 [M+1]. Anal. Calcd for $C_{19}H_{32}O_8$ (388): C, 58.75; H, 8.30. Found: C, 58.62; H, 8.46.

1.12. Methyl 2,3,5,6-tetra-*O*-acetyl-β-D-glucofuranoside (3d)

IR (neat): 3021, 2939, 2842, 1758, 1439, 1374, 1225, 1110, 1053, 930, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.00, 2.06, 2.08, 2.11 (4s, 12H, $4COCH_3$), 3.41 (s, 3H, OCH_3), 4.12–4.21 (dd, *J* = 12.2, 4.8 Hz, 1H), 4.46–4.53 (dd, *J* = 9.3, 5.1 Hz, 1H), 4.60–4.67 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.89 (br s, 1H), 4.99 (br s, 1H), 5.23–5.31 (m, 1H), 5.34 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR: δ 21.0 (2C), 21.1 (2C), 56.2, 63.6, 69.2, 73.8, 78.6, 80.7, 107.9, 169.6, 169.9 (2C), 170.9; $[\alpha]_D$ −32 (*c* 1.1, $CHCl_3$); *m*/*z*: 363 [M+1]. Anal. Calcd for $C_{15}H_{22}O_{10}$ (362): C, 49.72; H, 6.12. Found: C, 49.83; H, 6.25.

1.13. Ethyl 2,3,5,6-tetra-*O*-acetyl-β-D-glucofuranoside (3e)

IR (neat): 3030, 2933, 2847, 1760, 1441, 1370, 1229, 1105, 1055, 930, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.22–1.33 (t, *J* = 7.2 Hz, 3H), 2.00, 2.06, 2.07, 2.10 (4s, 12H, $4COCH_3$), 2.64–2.68 (q, 2H), 4.10–4.19 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.43–4.59 (m, 2H), 5.19–5.37 (m, 2H), 5.40–5.53 (m, 1H), 5.63 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR: δ 15.4, 20.8 (2C), 21.0 (2C), 25.8, 64.4, 69.2, 73.9, 78.3, 80.8, 106.5, 169.6, 170.1, 170.9; $[\alpha]_D$ −23.8 (*c* 1.1, $CHCl_3$); *m*/*z*: 377 [M+1]. Anal. Calcd for $C_{16}H_{24}O_{10}$ (376): C, 51.06; H, 6.43. Found: C, 50.88; H, 6.60.

1.14. Methyl 2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranoside (3f)

IR (neat): 3021, 2941, 2840, 2370, 1757, 1439, 1373, 1216, 1108, 1054, 925, 758, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.06, 2.09, 2.11, 2.14 (4s, 12H, $4COCH_3$), 3.38 (s, 3H, OCH_3), 4.11–4.40 (m, 3H), 4.92 (br s, 1H), 5.02 (d, *J* = 5.8 Hz, 2H), 5,35–5.42 (m, 1H); ^{13}C NMR: δ 19.9 (2C), 20.0 (2C), 54.3, 62.2, 69.1, 79.6, 80.8, 106.1, 169.7, 170.0, 170.2, 170.6; $[\alpha]_D$ −43 (*c* 1.1, $CHCl_3$); *m*/*z*: 363 [M+1]. Anal. Calcd for $C_{15}H_{22}O_{10}$ (362): C, 49.72; H, 6.12. Found: C, 49.85; H, 6.23.

1.15. Ethyl 2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranoside (3g)

IR (neat): 3020, 2946, 2835, 2367, 1760, 1441, 1375, 1219, 1108, 1050, 930, 758, 605 cm^{-1}; ^{1}H NMR

($CDCl_3$): δ 1.03–1.11 (t, $J = 7.4$ Hz, 3H), 1.90, 1.94, 1.96, 1.98 (4s, 12H, 4COCH_3), 3.29–3.45 (m, 1H), 3.50–3.66 (m, 1H), 3.95–4.04 (m, 1H), 4.06–4.10 (m, 2H), 4.15–4.23 (m, 1H), 4.84–4.88 (m, 2H), 5.18–5.23 (dt, $J = 4.6$ Hz, 1H); ^{13}C NMR: δ 15.2, 20.8 (2C), 21.0 (2C), 62.5, 62.8, 69.6, 76.8, 80.0, 81.8, 105.6, 169.9, 170.2 (2C), 170.7; $[\alpha]_D$ −28 (*c* 2.2, $CHCl_3$); *m/z*: 377 [M+1]. Anal. Calcd for $C_{16}H_{24}O_{10}$ (376): C, 51.06; H, 6.43. Found: C, 50.85; H, 6.57.

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